

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
10 May 2001 (10.05.2001)

PCT

(10) International Publication Number
WO 01/32556 A1

- (51) International Patent Classification⁷: C01B 3/40, 3/38 (74) Agents: ALLOCCA, Joseph, J. et al.; ExxonMobil Research and Engineering Company, P.O. Box 900, Annandale, NJ 08801-0900 (US).
- (21) International Application Number: PCT/US00/28698
- (22) International Filing Date: 17 October 2000 (17.10.2000) (81) Designated States (*national*): AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HR, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, SL, TR, TT, UA, UZ, VN, YU, ZA.
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
09/430,803 29 October 1999 (29.10.1999) US (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant: EXXON RESEARCH AND ENGINEERING COMPANY [US/US]; P.O. Box 900, 1545 Route 22 East, Annandale, NJ 08801-0900 (US).
- (72) Inventors: HOHN, Keith, L.; 2305 Treesmill Court, Manhattan, KS 66503 (US). SCHMIDT, Lanny, D.; 4852 13th Avenue South, Minneapolis, MN 55417 (US). REYES, Sebastian, C.; 9 Mohawk Trail, Branchburg, NJ 08876 (US). FEELEY, Jennifer, S.; 652 Plantation Ridge Drive, Baton Rouge, LA 70810 (US).
- Published:
— With international search report.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 01/32556 A1

(54) Title: PROCESS FOR CATALYTIC PARTIAL OXIDATION USING PARTICULATE CATALYSTS

(57) Abstract: Catalytic partial oxidation is effected in the presence of a supported, Group VIII metal catalyst by reacting a light hydrocarbon with an oxygen containing gas, the catalyst support being in a preferred size range.

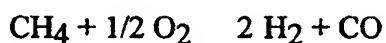
PROCESS FOR CATALYTIC PARTIAL OXIDATION USING PARTICULATE CATALYSTS

FIELD OF THE INVENTION

This invention relates to a catalytic partial oxidation process wherein a light hydrocarbon, e.g., methane, is converted to synthesis gas, carbon monoxide and hydrogen. More particularly, this invention relates to a particular particulate catalyst for the catalytic partial oxidation process.

BACKGROUND OF THE INVENTION

Catalytic partial oxidation is a known process wherein a light hydrocarbon, for example, a C₁-C₄ alkane or hydrocarbon, or more likely methane, as may be in or obtained from natural gas is converted catalytically in the presence of an oxygen containing stream to synthesis gas. The following stoichiometric equation exemplifies the reaction:



The reaction is particularly attractive in gas to liquids projects wherein natural gas is converted to synthesis gas, and the synthesis gas is converted to heavy hydrocarbons, C₂+, via the Fischer-Tropsch process. Because the stoichiometric reactant ratio for the Fischer-Tropsch process with non-shifting catalysts is about 2.1/1, the synthesis gas produced by catalytic partial oxidation is a particularly valuable feed for the Fischer-Tropsch process.

The catalytic partial oxidation process has been reported in a number of recently published patent applications, e.g., EP 0 576 096 A2. Nevertheless, there is a desire to improve both the yield and selectivity of the process, particularly regarding hydrogen selectivity, and thereby further the commercial prospects for the process.

SUMMARY OF THE INVENTION

The invention may be exemplified by a catalytic partial oxidation process comprising the reaction of a light hydrocarbon, e.g., a C₁-C₄ alkyl, preferably methane, by itself, or as a component of natural gas, with oxygen in the presence of a supported, Group VIII noble or non-noble metal catalyst, the support comprising particulate solids of a particular size range.

The prior art in the area of catalytic partial oxidation does not suggest that a particular particle size range exists in which the process becomes highly efficient with regard to hydrogen selectivity. The prior art suggests that while particulates may be used in the catalytic partial oxidation process, it is preferred to use monoliths or foams as the catalyst support. The reasoning being that foams, for example, readily conduct heat because of their bi-continuous structure, whereas particles only conduct heat at narrow point contacts, and therefore, are thought to have a lower overall axial thermal conductivity than foams or monoliths.

Nevertheless, the efficiency of the process and an aspect of this invention is the adequate management of both the heat conductivity, or heat flux along the catalyst bed and the number of active catalytic sites that can be placed on the external surface of the support per unit volume of the reactor.

Due to their large porosity, catalytic support materials, such as foams and monoliths have relatively poorer axial and radial heat conductivity than smaller particulates. Also, the number of active catalytic sites that can be placed on a support is proportional to the surface to volume ratio (S/V), i.e., the external, geometric surface to volume ratio of a granular material, excluding the intra particle surface area, and therefore, smaller and smaller particles would seem to be preferred. However, very small particles do not lend themselves to good heat conductivity in the bed, heat being transferred by point contacts and by radiation along in the catalyst bed. Consequently, there is a need to balance the competing aspects of the overall axial thermal conductivity of the bed with the surface density of catalytic sites in order to achieve the necessary process efficiency.

The surface area to volume (S/V) ratio (also referred to as the geometric surface to volume ratio) of a catalytic bed, e.g., a packed bed, can be readily determined from a knowledge of the particle size and the porosity of the particulate bed. For example, the S/V ratio of a packed bed of spherical particles or particles that can be assumed to be, or described as spherical, can be described by $S/V = 3(1 - \emptyset)/r_p$; where \emptyset is the porosity of the bed and r_p is the particle radius. Because packed beds can contain a range of particle sizes, the particle radius can be selected as the radius of the average particle size (i.e., volumetric average particle size). For packed beds, \emptyset ranges from about 0.3 to about 0.5 and the preferred surface to volume ratio is about $15\text{-}230\text{ cm}^{-1}$. However, a more preferred surface to volume range is $18\text{-}140\text{ cm}^{-1}$, more preferably $18\text{-}105\text{ cm}^{-1}$.

Preferred particles have a diameter ranging from about 200-2000 microns, more preferably about 400-1600 microns, and still more preferably about 400-1200 microns. The particles may be spherical or other shapes which can be described or approximated by a diameter and are generally described as being granular.

Thus, the process balances surface to area ratio, as that ratio has been defined, with the overall bed (or packing) thermal conductivity which is described in D. Kunii and J. M. Smith, *AIChE J.* 6(1), p. 71-78 (1960), incorporated herein by reference.

The catalyst support is generally a difficult to reduce refractory metal oxide, such as alumina, particularly alpha alumina, zirconia, titania, hafnia, silica, silica-alumina; rare earth modified refractory metal oxides, where the rare earth may be any rare earth metal, e.g., lanthanum, yttrium; alkali earth metal modified refractory metal oxides; and these materials may be generally categorized as materials having a substantially stable surface area at reaction conditions, for example, a surface area that is not substantially altered by reaction conditions, or altered in any way that affects the reaction.

Because thermal conductivity is one of the competing elements for the nature of the catalyst support, the support having better thermal conductivity can be used in the form of smaller average particle sizes. Nevertheless, the S/V ratios given above generally take this element into account and apply for all preferred supports, i.e., zirconia and alpha alumina, particularly preferred being alpha alumina, and rare earth stabilized alumina. The preferred support particles generally have a low total surface area, e.g., $<20 \text{ m}^2/\text{gm}$, and microporosity is not important to the process.

The catalytic metal is preferably a Group VIII noble metal, e.g., platinum, iridium, rhodium, osmium, ruthenium, although nickel may also be used as the catalytic metal. Rhodium, however, is most preferred as the catalytic metal.

The hydrocarbon feed is preferably a light alkane, e.g., C₁-C₄, most preferably methane or a gas containing substantial amounts of methane, e.g., natural gas.

The oxygen used in the catalytic partial oxidation process may be pure or substantially pure oxygen or an oxygen containing gas, e.g., air, or a mixture of oxygen with an inert gas. Substantially pure oxygen is preferred, and pure oxygen is still more preferred. Optionally, either the hydrocarbon feed or the oxygen stream, or both, may be mixed with steam. When steam is present, the steam to carbon ratio may be about 0 to 2.5, preferably about 0.2 to 1.5.

The ratio of hydrocarbon feed to oxygen in the reaction zone may range from about 0.45 to about 0.75 oxygen to carbon ratio, more preferably 0.45-0.55. There may be some carbon dioxide in the feed, as for example, from recycle gases or as a diluent. Generally, however, virtually no CO₂ is consumed, e.g., CO₂ conversion in the catalyst bed is less than about 10%, preferably less than about 5%. Consequently, there is essentially no synthesis gas formation via CO₂ reforming.

In an embodiment of the invention reaction temperature is achieved quickly at the inlet of the catalyst bed for best results. In a preferred embodiment, the process takes place in a thin reaction zone, e.g., at high (reaction) temperatures, preferably ≤ 5 particle diameters from the bed inlet, more preferably ≤ 3 particle diameters from the bed inlet. In this thin zone,

substantially all of the oxygen is consumed, preferably $\geq 90\%$ of the oxygen is consumed, more preferably $\geq 95\%$ of the oxygen is consumed in this zone.

The hydrocarbon synthesis process, also generally known as the Fischer-Tropsch process may be exemplified by contacting synthesis gas, hydrogen and carbon monoxide, with a suitable hydrocarbon synthesis catalyst, e.g., iron, cobalt, or ruthenium, iron being a preferred catalyst for low H_2/CO ratio synthesis gas, and cobalt and ruthenium, particularly cobalt, being preferred for higher, i.e., > 1.0 , ratios of H_2/CO synthesis gas. More preferably, a non-shifting catalyst, e.g., Co, is preferred, more preferably supported cobalt. While any reactor type, fixed bed, fluid bed, slurry bed, may be employed, slurry bubble columns, where injected synthesis gas provides all or at least a portion of the energy required for maintaining the catalyst dispersed (i.e., fluidized) in the bubble column, are preferred. See, for example, U.S. 5,348,982 incorporated herein by reference.

The catalyst can be prepared by any technique, and conventional techniques, e.g., impregnation, incipient wetness, spray drying, etc., and may be exemplified by: placing the particulate support in an aqueous solution of a desired catalytic metal, e.g., rhodium nitrate of appropriate concentration.

To yield a catalyst with suitable metal loadings, the impregnated support is removed from the metal solution, dried (at temperatures of up to about $125^\circ C$) to remove moisture, and calcined, usually in air, for example at temperatures of about 300 to $600^\circ C$. The metal loading is that which is catalytically effective, for example ranging from about 2-25 wt% metal, preferably about 3-20 wt% metal. The oxide is normally quickly reduced to the

elemental and active form of the metal in the course of the catalytic partial oxidation process.

The catalytic partial oxidation process is conducted at suitable reaction conditions, such as those described in prior patents and patent applications. Thus, pressures may range from 1-100 atmospheres, and feed is contacted with the catalyst at temperatures ranging from 400-1200°C, preferably 500-800°C. Typically, gas hourly space velocities may range from a low of about $\geq 300,000 \text{ hr}^{-1}$ to about 10,000,000 hr^{-1} or higher, preferably at least about 600,000 hr^{-1} , more preferably at least about 1,000,000 hr^{-1} , still more preferably at least about 1,300,000 hr^{-1} .

The following examples will illustrate this invention, but are not meant to limit, in any way, the invention.

CATALYST PREPARATION

Supports were alumina spheres with diameters of 400, 800, 1200 and 3200 μm . Packed beds were prepared using the spherical particles and the porosity, interparticle pore diameters, and S/V as follows:

<u>Sample Number</u>	<u>Particle Diameter (Microns)</u>	<u>Bed Porosity (\emptyset)</u>	<u>Interparticle Pore Diameter cm^{-1}</u>	<u>S/V</u>
E1	400	.42	193	87
E2	800	.44	419	42
E3	1200	.45	655	27.5
E4	3200	.48	1969	4.9

Where the interparticle pore diameter is calculated by $[2 \varnothing / (3 (1 - \varnothing))] [D_p]$, where D_p is the particle diameter.

Prior to use, the alumina particles were sintered to decrease the internal surface area to $< 15 \text{ m}^2/\text{gm}$ (i.e., 400 m: $6.9 \text{ m}^2/\text{gm}$; 800 m: $6.5 \text{ m}^2/\text{gm}$; 1200 m: $14.5 \text{ m}^2/\text{gm}$; 3200 m: $12.3 \text{ m}^2/\text{gm}$.)

Calcination involved heating from 120°C to 1000°C at $20^\circ\text{C}/\text{minute}$, 1000°C to 1200°C at $5^\circ\text{C}/\text{minute}$; calcine at 1200°C for 6 hours.

Rhodium was applied to the sintered particles by placing them in an aqueous solution of rhodium nitrate of a concentration to obtain the desired metal loadings. The solution containing the particles was dried overnight to remove moisture, and the particles were then calcined at 600°C for 6 hours.

<u>Sample</u>	<u>Rh, wt%</u>
E1	15.2
E2	8.3
E3	11.1
E4	12.0

For comparative purposes Rh catalyzed monoliths were also prepared. Two alumina based (92% Al_2O_3 , 8% SiO_2) monoliths were used: R1 having 45 ppi (pores per inch) with an average pore diameter of 420 m, R2 having 80 ppi with an average pore diameter of 210 m. Surface areas of each were $< 1 \text{ m}^2/\text{gm}$.

Rhodium was applied to each monolith using a technique similar to that described for particles. The monoliths were impregnated with rhodium nitrate and left to dry overnight. The procedure was repeated where necessary to

obtain the desired rhodium loadings. The monoliths were then calcined at 600°C for 6 hours.

CATALYST TESTING PROCEDURES

Rh catalyzed spheres and monoliths were tested in plug flow quartz reactors. In all tests, Fiberfrax insulation (Fiberfrax Durablanket, Carborundum) covered with aluminum foil, was wrapped around the outside of quartz reactor tubes in order to prevent radial heat losses. Catalyzed spheres were supported on a quartz frit inside the quartz reactor tube. Upstream of the catalyzed spheres a ceramic fiber mat (Nextel 312, a 3M product: 62% Al_2O_3 , 24% SiO_2 , 14% B_2O_3) was used to help prevent heat losses. Catalyzed monoliths were sandwiched between two uncatalyzed, blank 45 ppi alumina monoliths (Hi Tech Ceramics : 92% Al_2O_3 , 8% SiO_2) to help prevent heat losses. All monoliths were wrapped with Fiberfrax paper (Carborundum) to seal them tightly in the quartz reactor tube.

Feed gases, CH_4 , O_2 , and N_2 , were controlled with Brooks mass flow controllers (5850E flow controllers). Unless specified otherwise, 20% of the feed was N_2 and the CH_4/O_2 ratio was 2 to 1. Feed gases were premixed and fed to the catalyst at ambient temperature. Pressure was maintained at 2 psig. The reactor was ignited by placing a bunsen burner on the reactant tube with feed gases flowing. When the ignition temperature was reached, the bunsen burner was removed and insulation was placed over the quartz tube containing the catalyst as described above. Product gases (CO , H_2 , CO_2 , C_2H_2 , C_2H_4 , C_2H_6) and unconverted feed gases (CH_4 , O_2 , N_2) were analyzed with an HP 5890, Series II gas chromatograph. All mass balances closed within $\pm 5\%$, with error usually less than 3%.

EXAMPLE 1

The activity of catalyst E2 of the current invention was compared with reference catalyst R1. The table below shows methane conversion and H₂ and CO product selectivities for both catalysts under the following test conditions:

- No feed preheat
- CH₄/O₂ feed ratio of 2.0
- 20% N₂ diluent in feed
- E2 catalyst bed dimensions 14 mm D x 10 mm L
- R1 catalyst bed dimensions 18 mm D x 10 mm L
- Rh content in E2 catalyst bed: 0.154 g
- Rh content in R1 catalyst bed: 0.149g

COMPARISON OF CATALYSTS E2 AND R1

Catalyst	GHSV (hr ⁻¹)	% CH ₄ Conversion	% O ₂ Conversion	% H ₂ Selectivity	% CO Selectivity
E2	190,000	86.1	100	93.7	93.0
R1	118,000	78.8	100	89.5	95.8
E2	430,000	86.4	100	95.7	93.1
R1	400,000	68.2	98.4	78.1	92.6

The average pore diameter in each bed, i.e., using the sphere based E2 catalyst or the monolith based R1 catalyst, is the same (420 microns). Rh loadings in the reactor are also the same within < 4%.

The E2 catalyst clearly shows superior performance both in terms of catalyst activity and selectivity versus the R1 catalyst, particularly at high gas hourly space velocity (GHSV). The E2 clearly has much better performance at 400,000/hr and higher. While total C₂ formation was < 0.1% on both catalysts at low GHSV, at high GHSV the R1 catalyst made significantly more total C₂ products (i.e., 1.4% for R1 versus < 0.1% for E2). Also, oxygen conversion was 100% on the E2 catalyst at both space velocities, but only 98.4% on the R1 catalyst at 400,000/hr.

This example demonstrates the significant improvement in catalytic partial oxidation (CPO) activity and selectivity that can be achieved through the use of a sphere based versus a monolith based catalyst design at high gas hourly space velocities.

EXAMPLE 2

The activity of catalyst E1 of the current invention was compared with reference catalyst R2. The table below shows methane conversion and H₂ and CO product selectivities for both catalysts under the following test conditions:

- No feed preheat
- CH₄/O₂ feed ratio of 2.0
- 20% N₂ diluent in feed
- E1 catalyst bed dimensions: 14 mm D x 10 mm L
- R2 catalyst bed dimensions: 18 mm D x 10 mm L
- Rh content in E1 catalyst bed: 0.276g
- Rh content in R2 catalyst bed: 0.246g

COMPARISON OF CATALYSTS E1 AND R2

Catalyst	GHSV (hr ⁻¹)	% CH ₄ Conversion	% O ₂ Conversion	% H ₂ Selectivity	% CO Selectivity
E1	230,000	85.7	100	95.4	92.2
R2	170,000	82.8	100	89.8	95.6
E1	350,000	86.3	100	95.5	92.5
R2	380,000	53.7	96.6	57.0	82.9
E1	660,000	86.5	100	96.2	92.8

The average pore diameter in each bed, i.e., using the sphere based E1 catalyst or the monolith based R2 catalyst, is the about the same (192 and 210 microns respectively). Rh loadings in the reactor are also about the same, within 11%.

The E1 catalyst clearly shows superior performance both in terms of catalyst activity and selectivity versus the R2 catalyst at high gas hourly space velocity (GHSV). Where conversions and selectivities of the E1 and R2 catalysts are somewhat similar at ca. 200,000/hr; the E1 clearly has much better performance at higher space velocity. Comparison of the data above 300,000/hr shows a substantial drop off in performance for the R2 catalyst, versus high activity and selectivity for the E1 catalyst up to 660,000/hr in this example.

While total C₂ formation was < 0.1% on both catalysts at low GHSV (i.e., ca. 200,000/hr), at higher GHSV the R2 catalyst made significantly more total C₂ products than the E1 catalyst (i.e., 2.3% for R2 at 380,000/hr versus < 0.1% for E1 at 350,000/hr and 660,000/hr).

This example again demonstrates that significant improvement in catalytic partial oxidation activity and selectivity that can be achieved through the use of a sphere based versus a monolith based catalyst design at high gas hourly space velocities.

EXAMPLE 3

This example demonstrates that a range of sphere particle sizes are useful in the current invention. Representative steady state CPO activities and selectivities are shown below at a number of gas hourly space velocities (GHSV) for catalysts E1, E2, E3, and E4 of the current invention. In all tests, no preheat was used, CH₄/O₂ feed ratio was 2.0 and 20% N₂ was used as a diluent, unless otherwise noted.

E1 Catalyst Performance Data

GHSV (hr ⁻¹)	% CH ₄ Conversion	% H ₂ Selectivity	% CO Selectivity
230,000	85.7	95.4	92.2
660,000	86.5	96.2	92.8

E2 Catalyst Performance Data

GHSV (hr ⁻¹)	% CH ₄ Conversion	% H ₂ Selectivity	% CO Selectivity
190,000	86.1	93.7	93
660,000	86.3	94.1	93.1
1,800,000	85.8	94.8	94.6
2,300,000 *	84.4	95.0	95.2

* This test was carried out with 15% nitrogen in the feed.

E3 Catalyst Performance Data

GHSV (hr^{-1})	% CH ₄ Conversion	% H ₂ Selectivity	% CO Selectivity
190,000	84.2	93.8	91.1
660,000	85.3	93.9	92.2

E4 Catalyst Performance Data

GHSV (hr^{-1})	% CH ₄ Conversion	% H ₂ Selectivity	% CO Selectivity
94,000	81.0	95.0	91.8
166,000	79.2	91.2	92.4
400,000	70.5	84.8	90.7

Except on the E4 catalyst, total C₂ selectivity was < 0.1% and oxygen conversion was 100% within experimental error in all tests described above. For the E4 catalyst: at 94,000/hr, total C₂ selectivity was < 0.1% and oxygen conversion was 99.5%; at 166,000/hr, total C₂ selectivity was < 0.1% and oxygen conversion was 98.8%; and at 400,000/hr, total C₂ selectivity was < 1.05% and oxygen conversion was 97.1%.

EXAMPLE 4

This example demonstrates that catalyst beds containing Rh catalyzed spheres of more than one size are also effective CPO catalysts. The table below shows data on a 50/50 mixture (by weight) of catalysts E1 and E3. In these tests, no preheat was used, CH₄/O₂ feed ratio was 2.0 and 20% N₂ was used as a diluent. Total amount of Rh in the reactor used for these mixed bed runs was 0.223 g.

(50% E1 + 50% E3) Mixed Bed Catalyst Performance Data

GHSV (hr^{-1})	% CH ₄ Conversion	% H ₂ Selectivity	% CO Selectivity
190,000	83.8	93.2	90.8
660,000	85.0	95.6	91.5

CLAIMS:

1. A catalytic partial oxidation process comprising contacting a C₁-C₄ hydrocarbon feed with oxygen or an oxygen containing gas with a bed of particulate, supported, Group VIII metal catalyst, the support having a surface to volume ratio of about 15-230 cm⁻¹, and the particle size being about 200-2000 microns diameter.
2. The process of claim 1 wherein substantially all of the oxygen is consumed in a zone of ≤ 5 particle diameters from the feed inlet to the catalyst bed.
3. The process of claim 2 wherein $\geq 90\%$ of the oxygen is consumed in the zone.
4. The process of claim 2 wherein the surface to volume ratio is 18-140 cm⁻¹.
5. The process of claim 2 wherein the space velocity is $\geq 300,000$ hr⁻¹.
6. The process of claim 2 wherein the space velocity is $\geq 600,000$ hr⁻¹.
7. The process of claim 2 wherein the metal is rhodium.
8. The process of claim 2 wherein the support has a substantially stable surface area at reaction conditions.

9. The process of claim 8 wherein the support is selected from the group consisting of refractory metal oxides, rare earth modified refractory metal oxides, alkali earth metal modified refractory metal oxides.

10. The process of claim 2 wherein the feed comprises methane.

11. The process of claim 9 wherein a synthesis gas is produced and the synthesis gas is a feed to a cobalt catalyzed Fischer-Tropsch process.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/28698

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B3/40 C01B3/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX, API Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 303 438 A (DAVY MCKEE CORP) 15 February 1989 (1989-02-15) the whole document ---	1-11
X	EP 0 548 679 A (IDEMITSU KOSAN CO) 30 June 1993 (1993-06-30) examples ---	1
A	EP 0 576 096 A (SHELL INT RESEARCH) 29 December 1993 (1993-12-29) cited in the application the whole document --- -/--	1,5-7

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

8 document member of the same patent family

Date of the actual completion of the international search

17 January 2001

Date of mailing of the international search report

25.01.2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Van der Poel, W

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/28698

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>CHU Y ET AL: "PARTIAL OXIDATION OF METHANE TO CARBON MONOXIDE AND HYDROGEN OVER NIO/LA2O3/DELTA AI2O3 CATALYST" APPLIED CATALYSIS A: GENERAL, NL, ELSEVIER SCIENCE, AMSTERDAM, vol. 134, no. 1, 4 January 1996 (1996-01-04), pages 67-80, XP000199016 ISSN: 0926-860X page 69 -page 71</p>	1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 00/28698

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/SAJ 210

Continuation of Box I.2

Present claims 1-11 relate to a catalytic partial oxidation process defined (inter alia) by reference to the following parameter(s):

P1: the surface to volume ratio of the catalyst support
P2: the particle size of the catalyst

The use of these parameters in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameters the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to documents concerned with catalytic partial oxidation processes using particulate catalysts. In the search special attention has been given to documents concerned with particle size, porosity, specific surface area, pore volume etc., because these parameters influence the surface to volume ratio of the catalyst support as presently claimed.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/28698

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0303438 A	15-02-1989	AU 610219 B	16-05-1991
		AU 2098988 A	16-02-1989
		BR 8804093 A	07-03-1989
		CN 1031511 A,B	08-03-1989
		DK 453388 A	15-02-1989
		IN 171834 A	23-01-1993
		JP 1145301 A	07-06-1989
		NO 883567 A,B,	15-02-1989
		NZ 225819 A	26-02-1990
		SU 1831468 A	30-07-1993
		ZA 8805994 A	31-01-1990
EP 0548679 A	30-06-1993	AU 661742 B	03-08-1995
		AU 3002092 A	01-07-1993
		CA 2085315 A	21-06-1993
		JP 5221602 A	31-08-1993
		NO 924885 A	21-06-1993
		NZ 245394 A	28-03-1995
EP 0576096 A	29-12-1993	AT 173449 T	15-12-1998
		AU 4147193 A	06-01-1994
		BR 9302449 A	11-01-1994
		CA 2099083 A	25-12-1993
		CN 1081998 A,B	16-02-1994
		DE 69322129 D	24-12-1998
		DE 69322129 T	12-05-1999
		ES 2127241 T	16-04-1999
		JP 6092603 A	05-04-1994
		MX 9303766 A	31-01-1994
		NO 932313 A	27-12-1993
		NZ 247962 A	28-08-1995
		RU 2115617 C	20-07-1998
		ZA 9304505 A	18-01-1994